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(54) Title: PROCESS TO PREPARE 5-FORMYLVALERIC ACID

(57) Abstract

Process to separate linear 5-formylvaleric acid from a mixture of 5- and 3- and 4-formylvaleric acids, wherein the separation is performed by fractional extraction with two immiscible solvents of which one solvent is an aqueous solvent and the other solvent is an organic solvent, in which the organic solvent has a higher or lower affinity for 5-formylvaleric acid than its affinity for the 3-formylvaleric acids and for the 4-formylvaleric acid. Furthermore the invention relates to an improved process to prepare ε-caprolactam starting from a mixture of branched and linear formylvaleric acids or starting from pentenoic acid.

PROCESS TO PREPARE 5-FORMYLVALERIC ACID

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The invention relates to a process to separate
linear 5-formylvaleric acid from a mixture of 5- and 3-
and/or 4-branched formylvaleric acids. The invention also
relates to a process to prepare 5-formylvaleric acid
10   starting from pentenoic acid by hydroformylation.
Furthermore the invention relates to an improved
process to prepare ε-caprolactam starting from a mixture
of branched and linear formylvaleric acids or starting
from pentenoic acid.
15   It is known from DE-C-952442 that 5-
formylvaleric acid can be prepared by hydroformylation of
pentenoic acids, for example 3-pentenoic acid. When 5-
formylvaleric acid is prepared by hydroformylation
branched by-products (3- and/or 4-formylvaleric acid) are
20   also formed. Two methods for separating the linear 5-
formylvaleric acid from 3- and 4-formylvaleric acid are
described in DE-C-952442: (1) The mixture of branched and
linear acids can first be subjected to a reductive
amination. The resulting amide product mixture can be
25   separated in linear and branched amide products. (2) The
separation of 5-formylvaleric acid from the mixture can be
performed by esterification of the linear and branched
formylvaleric acids and a subsequent separation of the 5-
formylvalerate ester. By hydrolysis of the isolated 5-
30   formylvalerate ester 5-formylvaleric acid can be obtained.
A disadvantage of the first method is that a
nitrogen containing waste stream of branched amide
products is obtained which is difficult to dispose of.
Furthermore, 5-formylvaleric acid is not obtained as an
35   isolated product.
A disadvantage of the second method is that
several chemical reactions have to be performed to obtain
5-formylvaleric acid starting from pentenoic acid. Loss of
valuable product in these reactions and the need for extra

process equipment, and thus an extra investment makes this
process unattractive when performed on a large and
commercial scale.

The aim of the present invention is to provide a
process to separate 5-formylvaleric acid from its isomers,
3- and/or 4-formylvaleric acid, with a high yield to 5-
formylvaleric acid in a more simple process than the
process described in DE-C-952442.

This aim is accomplished in that the separation
is performed by fractional extraction with two immiscible
solvents of which one solvent is an aqueous solvent
(resulting in an aqueous phase) and the other solvent is
an organic solvent (resulting in an organic phase).
In this invention it is understood that two solvents are
immiscible when two separate phases form when the solvents
are mixed.

It has been found that with the process
according to the invention it is possible to separate the
linear 5-formylvaleric acid from this mixture with an
extraction process. This was unexpected. In particular
because the linear and the branched formylvaleric acids
have very comparable physical properties. The fact that an
extraction process can be used for solving this problem is
very advantageous because extraction processes are easily
applied in large scale processes.

A further advantage is that it is possible to
obtain relatively pure 5-formylvaleric acid in a high
yield calculated on the starting amount of 5-formylvaleric
acid in the (crude) mixture of formylvaleric acids.

Another advantage is that possible pentenoic
acid or valeric acid, can also be separated from the
linear 5-formylvaleric acid in the process according to
the invention. These compounds are the starting compound
and a possible by-product respectively of the
hydroformylation process to prepare 5-formylvaleric acid.
Thus an additional separation of 5-formylvaleric acid and
pentenoic acid and/or valeric acid is not needed if these

products are present.

It has been known to prepare 5-formylvaleric
acid by hydrolysis of the corresponding methyl 5-
formylvalerate as described in US-A-4730040. A
5   disadvantage of this process is that methanol is obtained
as a by-product and that the yield of the hydrolysis to
5-formylvaleric acid, as shown in the examples of
US-A-4730040, is too low for a commercially interesting
process. The methyl 5-formylvalerate is preferably
10   prepared by hydroformylation of a methyl pentenoate ester
which is preferably prepared by carbonylation of butadiene
with methanol. By preparing the pentenoic acid by
carbonylation of butadiene with water, followed by the
preparation of the formylvaleric acid by hydroformylation
15   of the pentenoic acid the use of methanol or any other
alkanol is avoided. Moreover with the present invention it
is possible to prepare and isolate 5-formylvaleric acid in
less process steps starting from butadiene.

The aqueous solvent used in the process
20   according to the invention may be optionally a mixture of
water and another solvent which is miscible with water and
has a low solubility in the organic solvent of the other
phase such that two separate phases are formed. Preferably
water is used as the aqueous solvent.
25   The organic solvent used in the process
according to the invention may be any organic solvent
which has a higher or lower affinity for 5-formylvaleric
acid (5FVA) than its affinity for both the 3- and the 4-
formylvaleric acids (3FVA + 4FVA). In describing the
30   present invention, it may be useful to use the partition
coefficient K as a measure for the above mentioned
affinity:

$$35 \quad K_{acid} = \frac{[acid]_{organic\ phase}}{[acid]_{water\ phase}} \quad\quad\quad (1)$$

in which [acid] is the concentration of the specific

formylvaleric acid in the specific phase in mol/l. In order to achieve the benefits of the present invention, the K for 5FVA is smaller or greater than the K for 3FVA and the K for 4FVA. If the K for 5FVA is greater than the K for 3FVA and 4FVA the 5FVA will be obtained dissolved in the organic solvent after the extraction according to the invention. In general the K for 5FVA is smaller and the isolated 5FVA will be obtained in the water solvent after the extraction according to the invention. For practical reasons the K for 5FVA is preferably at least 1.5 times larger or smaller than the average K for 3- and 4FVA.

The organic solvent and water are subtantially immiscible. Some quantities of the other solvent will usually dissolve in the other phase in practice. With substantially immiscible is therefore meant that the mutual solubility is not higher than 10 wt.%.

Examples of suitable organic solvents are methyl tert-butyl ether, butyl acetate and nitrobenzene. Preferred solvents have a normal boiling point between 30 and 200°C.

It has been found that suitable organic solvents are those solvents which have a similar polarity, polarisability and H-bond formation character as nitrobenzene or more preferably methyl tert-butylether (MTBE). Examples of suitable solvents with these similar properties as MTBE are most esters and ethers. Examples of organic solvents which are less suitable, and which do not have a similar polarity, polarisability and H-bond formation character of MTBE or nitrobenzene, are alcohols, for example benzylalcohol, dodecanol, aromatic solvents, such as benzene and toluene, carboxylic acids, such as acetic acid, alkanes, such as n-heptane. However extraordinary alcohols, aromatic solvents and carboxylic acids may be similar to MTBE or nitrobenzene as described above. The qualitative terminology of similar polarity, polarisability and H-bond formation can be quantified in the following manner:

Solvents similar to MTBE have the following characteristics:

$$-2.8 < A < -0.2 \text{ and } 0.14 < B < 2.39 \qquad (2)$$

Solvents similar to nitrobenzene have the following characteristics:

$$1.7 < A < 4.0 \text{ and } -4.0 < B < -1.64 \qquad (3)$$

Preferably in formula (2) and (3):

$$B < -1.12 * A + 0.96 \text{ and}$$
$$B > 0.965 * A - 1.033 \qquad (4)$$

in which, A and B are a function of the solvent properties:

$$
\begin{aligned}
A = \quad & 0.23 * (T_B - 138.54)/62.36 + && (5)\\
& 0.24 * (\rho - 935.64)/184.82 + \\
& 0.0554 * (n_d - 1.4370)/0.0635 + \\
& 0.3916 * (\varepsilon_r - 15.02)/18.66 + \\
& 0.1208 * (\delta_d - 16.68)/1.738 + \\
& 0.4135 * (\delta_p - 6.11)/5.16 + \\
& 0.3462 * (\delta_h - 8.05)/6.97 + \\
& 0.4177 * (\delta - 20.69)/5.087 + \\
& 0.3370 * (\mu - 1.73)/1.20 + \\
& 0.3723 * (E_{T(30)} - 41.14)/7.61
\end{aligned}
$$

$$
\begin{aligned}
B = \quad & -0.3009 * (T_B - 138.54)/62.36 - && (6)\\
& 0.3882 * (\rho - 935.64)/184.82 - \\
& 0.5914 * (n_d - 1.470)/0.0635 + \\
& 0.1225 * (\varepsilon_r - 15.02)/18.66 - \\
& 0.5506 * (\delta_d - 16.68)/1.738 + \\
& 0.0970 * (\delta_p - 6.11)/5.16 + \\
& 0.2291 * (\delta_h - 8.05)/6.97 + \\
& 0.0583 * (\delta - 20.69)/5.087 +
\end{aligned}
$$

$$0.0381 * (\mu - 1.73)/1.20 +$$
$$0.1550 * (E_{T(30)} - 41.14)/7.61$$

in which T_B represents the normal boiling point (°C), ρ
the density measured at 20°C (kg/m^3), n_d the refractive
index (-), ε_r the dielectric constant measured at 20°C
(-), δ_d the Hansen solubility parameter of dispersion
(MPa$^{\frac{1}{2}}$), δ_p the Hansen solubility parameter of polarity
(MPa$^{\frac{1}{2}}$), δ_h the Hansen solubility parameter of hydrogen
bonding (MPa$^{\frac{1}{2}}$), δ the Scatchard-Hildebrand solubility
parameter (MPa$^{\frac{1}{2}}$) μ the dipole moment (Debey) and $E_{T(30)}$ the
Lewis donor/acceptor property (kcal/mol) (all properties
of the organic solvent).

The values for the above described properties
for most of the generally applied solvents can be found in
the following references: Properties of liquids and gases,
fourth edition, Reid, Prausknitz & Poling, Mc-Graw Hill,
1987; Properties of polymers (Their correlation with
chemical structure), D.W. van Krevelen, Elsevier
Scientific Publishing Company, Amsterdam 1990; Solvents
and Solvent Effects in Organic Chemistry, Ch. Reichardt,
VCH Verlagsgesellschaft mbH, Weinheim (Germany, FRG, 1990)
and DIPPR - Tables, Physical and thermodynamic properties
of pure components, Daubert & Danner, Taylor & Francis,
1994.

Examples of organic solvents which are within
the A-B space as described by the formula's above are
(solvent (A,B)), methyl tert-butylether (-2.2, 1.7),
butylacetate (-1.09, 0.62), nitrobenzene (2.09,-2.08), di-
ethylether (-2.42, 2.01), ethyl tert-butylether (-2.13,
1.51), methyl acetate (-0.82, 1.38), ethyl acetate (-1.01,
1.06), di-ethylketone (-0.39, 1.01) or di-isopropylketone
(-0.97, 0.72).

Typical examples of less suitable solvents are
benzylalcohol (1.53, -1.65), dodecanol (0.11, -0.44),
benzene (-2.17, -1.36), toluene (-1.95, -1.29), n-heptane
(-3.2, 0.83). The A and B values of these less suitable

solvents fall outside the ranges of the above formula's.

As mentioned before another group of suitable organic solvents are ethers and esters with 2 to 10 carbon atoms. This group of ethers and esters is not necessarily restricted to the A-B space as described above. The ethers and esters can be represented by the following formula

$$R^1-O-R^2 \qquad\qquad\qquad (7)$$

$$R^3-O-\underset{\underset{O}{\|}}{C}-R^4 \qquad\qquad\qquad (8)$$

in which R^1, R^2, R^3 and R^4 — independently — can be an alkyl, aryl group with 1 to 7 carbon atoms and in which R^1 and R^2 can be one divalent group. Preferably at least R^1 in the ether compound is an alkyl group. Preferably at least R^3 or R^4 is an alkyl group in the ester compound. Examples of ethers are methyl tert-butyl ether, ethyl tert-butylether, diethylether, diisopropylether, dibutylether, dipropylether, anisol or tetrahydrofurane. Examples of possible esters are butyl acetate, propylacetate, ethylacetate, methylacetate, ethylbutyrate, methylbutyrate, methylpropionate, ethylpropionate or propylpropionate.

Ethers are prefered over esters because esters can transesterify with the formylvaleric acid in which mixed esters are formed which is disadvantageous.

Figure 1 is a schematic representation of a fractional extraction performed in a gravity separated extractor as will be further described below.

Figure 2 is a schematic representation of a process in which pentenoic acid is converted in several steps to ε-caprolactam comprising a hydroformylation section (A+H) an extraction process according to the invention (C + D + optionally B) combined with an upgrading section (G+E) and a caprolactam-end section (F). The combination of these sections in this figure is not

meant to limit the present invention to this integral
process for the preparation of ε-caprolactam.

The separation of 5-formylvaleric acid from the
crude mixture of formylvaleric acids is performed by a
5   fractional extraction according to the invention. In
general, this fractional extraction merely involves the
intimate contact of an impure material with both phases of
the fractional extraction, which phases are substantially
immiscible, such that the impurities are preferentially
10   dissolved in one of the phases and the material being
purified (5FVA) is dissolved in the other phase.
Preferably the initial aqueous and organic solvent are
used in a substantially pure form. With pure form is meant
that no or almost no formylvaleric acids are present. The
15   material being purified is then recovered from solution in
its particular phase. The recovered 5FVA product will
contain less 3FVA and 4FVA impurities than the crude
mixture. The process can be performed discontinuously but
is preferably performed continuously.
20   The extraction performance can be further
improved by using an extraction enhancing agent. Examples
of these agents are bases or complexing agents. In the
process of the present invention the separation can
however be performed without using these agents. By
25   leaving out these enhancing agents a more simple process
is obtained.

The temperature and pressure at which the
fractional extraction is performed is not critical. In
general the next ranges are suitable. The pressure of the
30   extraction is preferably between 0.1 and 0.5 MPa. The
temperature of the extraction is preferably between 20°
and 100°C. Generally the temperature is lower than the
boiling point of the organic solvent at the used pressure.

Any of the known methods for accomplishing a
35   fractional extraction with two solvents may be utilized to
carry out the present invention. For example, mixer-
settlers may be used where crude formylvaleric acid

mixture is merely added to a vessel containing both
solvent phases of the fractional extraction system and
then the mixture is agitated vigorously to accomplish
intimate contact of the crude formylvaleric acids with

5   each of the two solvent phases. One of the solvents can
contain the crude formylvaleric acids. After sufficient
mixing, the phases are allowed settle out through gravity
or through the use of a centrifuge.

        If both a high purity and high yield of 5-

10   formylvaleric acid is required the process according to
the invention is preferably performed continuously in
which the mixture of formylvaleric acids is contacted with
the two extraction solvents in a plurality of contacting
stages.

15   Such a continuous process is characterized in
that continuously the initially aqueous solvent and
initially pure organic solvent are contacted counter
currently in various contacting stages in which the crude
mixture of formalvaleric acids is continuously fed at an

20   intermediate stage.

        An example of a preferred continuous fractional
extraction is accomplished in a gravity separated
extractor comprising some sort of vertical column (see
also Figure 1) which generally contains packing, baffles

25   or trays in order to increase the efficiency of the
extraction. In using such columns the crude formylvaleric
acids will preferably be fed to the column at a midpoint
thereof (5') while the pure (heavy) aqueous phase will be
fed to an upper point in the column (10) and above the

30   feed point of the crude formylvaleric acids. The pure
(lighter) organic solvent phase will be fed to a lower
point in the column (12) and below the feed point of the
crude formylvaleric acids. By force of gravity the lighter
phase will migrate countercurrently upwardly dissolving

35   the branched formylvaleric acids (in case the K of 5FVA is
smaller than the K of 3FVA and 4FVA. This situation shall
also be discussed below) and will be removed overhead

(11). The heavier phase will migrate downwardly through the column dissolving the 5-formylvaleric acid and will be removed as bottoms from the column (13).

The gravity separated extractor is normally a
5   cascade like apparatus (C+D). The feed point of the crude formylvaleric acid divides the cascade in an enriching section (D) and in a stripping section (C) (the letters and numbers refer to apparatus and streams as described in Figure 1 and 2).

10   The enriching section (D) is generally a vertically placed extraction column with between 5 and 100 and preferably between 10 and 40 theoretical separation stages. The stripping section (C) is also generally a vertically placed extraction column with between 5 and 100
15   and preferably between 10 and 40 theoretical separation stages. The two sections may form one column or may be split in two (or more) columns.

The crude mixture formylvaleric acid can be in a liquid form as such or dissolved in a solvent. Normally
20   this solvent is water or the organic solvent which is used in the fractional extraction. In a continuous process using a gravity separator the concentration of the crude formylvaleric acids in the feed is preferably between 20 and 100 weight percentage. A lower concentration will
25   generally result in economically unattractive dimensions of the stripping (C) and enriching (D) sections.

Preferably the concentration of formylvaleric acids is as high as possible (provided phase separation at the feed point still occurs) at the feed point (plate) in
30   the gravity separated extraction column. To accomplish this optimal formylvaleric acid concentration, which is for example around 50-60 weight% when MTBE is used as organic solvent, it can be usefull to separate some of the solvent present in the feed or solvent leaving the
35   enrichment section and before entering the stripping section. The concentration of formylvaleric acids at the feed point (plate) is the average concentration of streams

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(7) and (9). An example of such solvent separation is given in Fig. 2: In separator B organic solvent of stream (8) leaving the enrichment section and organic solvent of the feed (5) is separated (6) and the concentrated mixture
5   (7) is fed to the stripping section (C).

The solvent separation in (B) can for example be performed in one flash or simple distillation step at a pressure of between 0.1 and 0.5 MPa.

The aqueous and organic solvent volume flow
10   rates defined by the following formula's

$$1/K_{5FVA} * [10]/[7] \tag{9}$$
and
$$K_{3FVA} * [12]/[9] \tag{10}$$
15   and
$$K_{4FVA} * [12]/[9] \tag{11}$$

are preferably larger than 1 and more preferably between 1.1 and 2, in which [10], [7], [12] and [9] are the
20   respective volumetric flow rates of the water and organic solvent phases entering the stripping and enrichment sections corresponding with flows (10), (7), (12) and (9) (as shown in Fig. 2).

The lighter organic phase obtained overhead (11)
25   can be further processed in order to obtain substantially purified organic solvent (14) and branched formylvaleric acid (15). When the crude mixture is obtained in a hydroformylation of pentenoic acid, valeric acid and/or pentenoic acid are also obtained overhead. The purified
30   organic solvent (14) can be recycled to the fractional extraction column (10). The organic solvent (14), the branched formylvaleric acid (15), unconverted pentenoic acid (17) and valeric acid and other byproducts (16) of the hydroformylation can be obtained in separate flows by
35   for example distillation. The branched formylvaleric acids may be further processed, for example by a decarbonylation, in which the starting compound of the

hydroformylation, pentenoic acid, is obtained. The
unconverted pentenoic acid can advantageously be used as
starting compound (17) in a hydroformylation (A) to
prepare 5-formylvaleric acid. The aqueous phase (13), rich

5   in 5-formylvaleric acid, leaving the enrichment section
(D) can be further processed, so that substantially pure
5-formylvaleric acid is obtained. For example, 5-
formylvaleric acid can be separated from the mixture by
crystallization or more preferably by distillation or

10   extraction with an organic solvent. This organic solvent
can for example be the organic solvent used in the dual
solvent extraction, but also other organic solvents may be
used. Examples of other suitable solvents are benzene,
toluene or xylene.

15   The linear 5-formylvaleric acid can be
advantageously used as starting compound for the
preparation of adipic acid by (quantitative) oxidation.
Adipic acid is an Nylon-6.6 intermediate.

          Another example of a very interesting use is the
20   reductive amination of the 5-formylvaleric acid to 6-
aminocaproic acid and the subsequent cyclization to ε-
caprolactam. ε-caprolactam is a precursor for nylon-6. The
reductive amination of 5-formylvaleric acid and the
cyclization to ε-caprolactam is for example described in

25   the above mentioned DE-C-952442 and US-A-4730040. The
reductive amination may be performed in any suitable
solvent in which the 5-formylvaleric acid is soluble.
Examples of these solvents are water, ammonia, C_1-C_6
alkanols, for example methanol, ethanol, propanol or

30   butanol, ethers, for example diethyl ether, methyl tert-
butyl ether, dipropylether or diisopropylether. Ethers are
solvents because 5-formylvaleric acid can be easily
extracted from the aqueous phase with an ether. More,
prefered water is used as the solvent because the 5-

35   formylvaleric acid is obtained dissolved in water after
the fractional extractional. Optionally part of this water
(18) is separated from the aqueous mixture before the

reductive amination. Preferably this separation of water
is performed by distillation, and more preferably by
effect evaporation. In an effect evaporation water is
separated in two or more units in which each unit is
5   operated at a lower pressure than the prior unit and in
which the evaporated water (steam) of a prior unit is
condensed in a further unit, thereby supplying the heat
necessary to evaporate water in the further unit.

        With reductive amination is meant the reaction
10   of the 5-formylvaleric acid with a molar excess of ammonia
and hydrogen. The reductive amination is generally
performed in the presence of a group 8-10 metal containing
(hydrogenation) catalyst, for example Ni, Co, Ru, Pt or
Pd. Examples of specific hydrogenation catalysts are Raney
15   nickel, Raney cobalt and supported Ru catalysts for
example Ru on carbon or Ru on alumina. Ammonia is present
in a 2 to 50 fold molar excess. The pressure is super
atmospheric, preferably between 0.5 and 30 MPa. The
temperature is generally between 40 and 150°C. The
20   catalyst may for example be present as a slurry or fixed
in a packed bed. The reductive amination may for example
be performed in a tube reactor or a continuously stirred
tank reactor.

        The cyclization is preferably performed in the
25   same aqueous mixture as used in the reductive amination.
Other possible solvents are C_1-C_6 alkanols. The cyclization
is carried out in a separate step after the reductive
amination. Preferably the catalyst of the reductive
amination is not present during the cyclization. The
30   temperature of the cyclization step is generally between
150 and 370°C and preferably above 260°C. The cyclization
may for example be performed in a tube reactor or in a
continuously stirred tank reactor. After cyclization of 6-
aminocaproic acid to ε-caprolactam the ε-caprolactam (21)
35   and water (20) can be separated by for example
crystallization or preferably distillation or extraction.

        The crude mixture containing linear and branched

formylvaleric acids can be, for example, obtained by
hydroformylation of a pentenoic acid. The hydroformylation
reaction, in which the pentenoic acid reacts with carbon
monoxide and hydrogen, will in general/preferably be
5   performed in the presence of a homogeneous catalyst
system. However heterogeneous hydroformylation catalyst
systems may also be used. The catalyst system will
comprise a Group VIII metal of the Periodic Table of
Elements. Preferred metals are Co, Ru, Rh, Pd, Ir and Pt.
10   In DE-A-3628664 a Rh-triphenylphosphine catalyst system is
described for the preparation of formylcarboxylic acids by
hydroformylation. For the specific preparation of
formylcarboxylic acids and especially 5-formylvaleric acid
by hydroformylation not many catalyst systems are
15   described in literature. However the known catalyst
systems for hydroformylation in general, based on the
above described metals are in most cases suitable for this
reaction.

          Prefered hydroformylation processes to prepare
20   5-formylvaleric acid are performed in an aqueous reaction
mixture, because the pentenoic acid dissolves well in such
an aqueous mixture. When performing the reaction in an
aqueous reaction mixture the starting compound may also be
a pentenoate ester. The ester group will - during the
25   hydroformylation reaction - undergo hydrolysis to the acid
group by which the formylvaleric acid will be formed.
Preferably the catalyst systems of these processes have a
greater solubility in water than the branched and linear
formylvaleric acids when extracted with a suitable
30   solvent. This is advantageous because the catalyst system
can then be easily separated from the crude formylvaleric
acids by extraction (H). Preferably the extraction is
performed with the same organic solvent as used in the
fractional extraction in the process according to the
35   invention. The aqueous mixture still containing the
catalyst system (3) also obtained in such an extraction
(H) can be advantageously recycled to the hydroformylation

(A).

An example of such a catalyst system is a
rhodium based catalyst system combined with water soluble
bidentate phosphine ligands. Such a catalyst system is for
5   example described in WO-A-9426688.

Preferably a catalyst system is used comprising
platinum or a platinum compound and a water soluble
organic bidentate ligand. It has been found that, apart
from the above mentioned advantages, a hydroformylation
10 process using such a catalyst system will result in a high
selectivity to the linear 5-formylvaleric acid.

Preferably, the water-soluble compound used as
bidentate ligand may be represented by the following
general formula:

15

$$R^5R^6-M^1-R-M^2-R^7R^8 \qquad\qquad (12)$$

where M^1 and M^2 represent a phosphorus (P) atom, an
antimony atom or an arsenic atom, R represents a divalent
20 organic bridging group having at least three atoms and
where R^5, R^6, R^7 and R^8 represent the same or different
organic groups and where R^5, R^6, R^7, R^8 and/or R comprise
at least one hydrophilic group. It is preferred for M^1 and
M^2 to be phosphorus (P) atoms.

25   The hydrophilic group may be any group which
increases the solubility of the organic bidentate ligand
in water. This hydrophilic group may be a strongly polar
group, for example amine derivatives, for example
dialkylamine groups or more preferably a ionic group. The
30 position of the hydrophilic group in the ligand compound
is not critical. The hydrophilic group may be linked to
the groups R^5-R^8 or to the bridging group R.

Examples of suitable ionic hydrophilic groups
are a sulphonate group, $-SO_3Z$, a phosphonate group $-PO_3Z$, a
35 carboxylate group, $-COOZ$, or a monovalent cationic group
of an ammonium salt $-N(R^9)_3X$, where Z represents a
monovalent cationic group, R^5 an aliphatic or aromatic

hydrocarbon group having from 1 to 18 carbon atoms or
hydrogen and X represents an anionic group. If the
bidentate ligand contains aryl groups, for example for R^5,
R^6, R^7 and/or R^8, the cationic group of an ammonium salt
5   preferably is bonded to a non-aryl group in the bidentate
ligand. These non-aryl groups can be the bridging group
(R) or the non-aryl groups for R^5-R^8. Another example of a
hydrophilic group is a phenolate group Ar-OZ, present in
the ligand. The Ar group may be any (aromatic) group R^5,
10   R^6, R^7, R^8 and/or R.

Examples of suitable cationic groups (Z) are the
inorganic cations of metals, especially of alkali and
earth alkali metals, for example sodium, potassium,
calcium and barium as well as quaternary ammonium ions,
15   for example tetramethylammonium, tetrapropylammonium or
tetrabutylammonium.

Examples of suitable anionic groups (X) are
halides, sulphate and phosphate groups and R^{10}-SO_3^-, R^{10}-
CO_2^- and R^{10}-PO_3^- groups, where R^{10} represents a C_1-C_{12} alkyl
20   or C_1-C_{12} aryl.

In general, the number of hydrophilic groups is
between 1 and 6. It is preferred for the number of groups
to be between 1 and 4 per molecule of bidentate ligand.

R^5, R^6, R^7 and R^8 may be C_1-C_{15} (cyclo)alkyl
25   groups or C_5 -C_{20} aryl groups. These groups preferably are
aryl groups such as naphthyl, phenyl or a heterocyclic
aryl group such as pyridyl. Examples of possible
substituents are alkyl groups, for instance a methyl,
ethyl or isobutyl group, alkoxy groups, for instance
30   methoxy, ethoxy, isopropoxy and halides.

Bridging group R may be an organic group with 3-
30 carbon atoms. R may be a divalent C_3-C_{12} alkyl group,
for example trimethylene, tetramethylene, pentamethylene
or hexamethylene.

35   Examples of bidentate phosphine ligand compounds
according to formula (9) without the hydrophilic group are
1,3-bis(diphenyl-phosphino)propane, 1,4-bis(diphenyl-

phosphino)butane, 2,3-dimethyl-1,4-bis(diphenylphosphino)-
butane, 1,4-bis(dicyclohexylphosphino)butane, 1,3-bis(di-
p-tolyl-phosphino)propane, 1,4-bis(di-p-methoxyphenyl-
phosphino)butane, 2,3-bis(diphenylphosphino)-2-butene,
5   1,3-bis(diphenylphosphino)-2-oxopropane and 2-methyl-2-
(methyldiphenylphosphino)-1,3-di(diphenylphosphino)-
propane. The above ligands, when substituted with one or
more hydrophilic group, are examples of possible water-
soluble bidentate ligand compounds used in the process
10   according to the invention.
        Preferably the bridging group R forms a "rigid"
link between M^1 and M^2. By a "rigid" link is meant a link
that allows M^1 and M^2 little or no conformational freedom
relative to one another (comparable to a double bond,
15   which also allows little conformational freedom)
irrispective of which groups R^5-R^8 are present. It has been
found that bidentate phosphine ligand compounds having a
bridging group that allows more conformational freedom
yield less favourable results. Preferably the shortest
20   distance between M^1 and M^2 is formed by 3, 4 or 5 atoms.
These atoms may represent, besides carbon, a heteroatom
such as the nitrogen, oxygen, sulphur and phosphor atoms.
        Example of suitable "rigid" bridging groups are
divalent organic groups containing at least one cyclic
25   group in the chain between M^1 and M^2, which cyclic group
may be aromatic. This cyclic group imparts the "rigid"
properties to the bridging group and may possibly be
linked to M^1 and/or M^2 via an alkyl group having from 1 to
3 carbon atoms. An example of suitable bridging groups may
30   be represented by the following general formula:

$$- R^{11} - Y - R^{12}-\qquad\qquad (13)$$

where Y represents a hydrocarbon group, which group
35   contains at least one cyclic structure (which cyclic
structure imparts rigidity to the bridge group), the
cyclic structure optionally being substituted and which

hydrocarbon compound may contain heteroatoms such as
oxygen, nitrogen, phosphorus and sulphur and where R^{11} and
R^{12} may independently of one another be omitted or may
independently of one another represent a C_1-C_3 alkylene
group. Preferably, the cyclic structure will contain from
3 to 20 atoms. M^1 and M^2 may be cis or trans to the rigid
ring Y. If a group R^{11} and/or R^{12} is/are present, it/they,
too, may be cis or trans to the rigid bridge Y.

An example of a bidentate phosphine having a
cyclic structure in Y which contains a heteroatom is 2,3-
o-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)-
butane (DIOP), which is commercially available. Compounds
derived from DIOP are also suitable. Another group of
cyclic structures for Y in formula (13) are cyclic alkanes
such as cyclopropane, cyclobutane, cyclopentane and
cyclohexane. Bridged cycloalkanes, too, are highly
suitable to be used as cyclic group Y in formula (13).
Examples of such bridged cycloalkanes are
bicyclo[1,1,2]hexane, bicyclo[2,2,1]heptane and
bicyclo[2,2,2]octane.

The cyclic structure of Y may optionally be
substituted with one or more aryl or alkyl groups and/or
with other functional groups. The functional groups
substituted on Y may also be hydrophilic groups which
increases the solubility of the organic bidentate ligand
used in the process according to the invention. The
functional groups may optionally be used for immobilizing
the bidentate phosphine on a carrier. Examples of these
functional groups are, for instance, carbonyl, hydroxyl,
amine and halide groups.

Other suitable "rigid" bridging groups are
divalent organic groups containing (at least) 2 coupled,
preferably aromatic, ring systems. The two ring systems
have a hindered rotation relative to one another, as a
result of which the bridges possess 'rigid' properties.
Such compounds are described in detail in, for instance,
"Advanced Organic Chemistry, Reactions, Mechanisms and

Structure", Jerry March, 4th ed. 1992, John Wiley & Sons,
page 101. Examples of suitable coupled ring systems are
biphenyl, binaphthyl and bipyridyl. An example of a
bidentate phosphine with a "rigid" bridge group with

5   coupled ring systems is 2,2'-bis-(diphenylphosphino)-1,1'-
binaphthyl (BINAP), which is commercially available. The
ring systems may be substituted in the same way as the
cyclic structure Y described above.

A completely different group of suitable "rigid"

10   bridging groups R with cyclic compounds are bis(η-
cyclopentadienyl)- coordination compounds of metals (also
known as metallocenes). A particularly suitable
metallocene is ferrocene.

Examples of suitable bidentate phosphines with

15   rigid bridging groups (R) into which hydrophilic groups
have not yet been incorporated are the earlier mentioned
DIOP, bis(diphenylphosphine)ferrocene, trans-1,2-bis(di(m-
methylphenyl)phosphinomethyl)cyclobutane, trans-
[(bicyclo[2.2.1]heptane-2,3-diyl)bis(methylene)]-

20   bis[diphenylphosphine], trans-[(bicyclo[2.2.2]octane-2,3-
diyl)bis(methylene)]-bis[diphenylphosphine], trans-1,2-
bis(diphenylphosphinomethyl)cyclobutane (DPMCB), trans-
1,2-bis[diphenylphosphinomethyl]trans-3,4-
bis[phenyl]cyclobutane and the earlier mentioned BINAP.

25   The hydrophilic groups can readily be linked to
the above-mentioned compounds. Sulphonate groups, for
instance, can be bonded to the ligand via sulphonation
with the aid of SO_3 in sulphuric acid. Carboxylate groups,
phosphonate groups and cationic radicals of an ammonium

30   salt can be incorporated using synthesis processes known
in the art.

Platinum or the platinum compound can be applied
in a homogeneous system or a heterogeneous, immobilized
system. Homogeneous systems are preferred. Since platinum

35   forms a complex with the bidentate compound in situ, the
choice of an initial Pt compound is not generally
critical. Suitable platinum compounds are for example

salts of platinum with, for instance, hydrogen halides,
nitric acid, sulphonic acid and carboxylic acids having
not more than 12 carbon atoms per molecule. Examples of
such salts are $PtCl_2$, $Pt(AcAc)_2$ (AcAc= acetylacetonate),
5      $CODPtCl_2$ (COD= cyclooctadiene), $Pt(CH_3CN)_4(BF_4)_2$ and
$CODPt(AcAc)BF_4$.

The temperature of the hydroformylation is in
general between 50 and 200°C and preferably between 90 and
120°C.

10   The pressure is not critical and may e.g. be
between 4 and 20 MPa.

The molar ratio of hydrogen to carbon monoxide
may e.g. be between 1:10 and 10:1. This ratio affects the
ratio of the yield of formyl carboxylic acids to the yield
15   of dicarboxylic acids. The dicarboxylic acids content of
the resulting reaction mixture will increase as more
carbon monoxide is used. If the desired product is formyl
carboxylic acid, the molar ratio of carbon monoxide to
hydrogen will be about 1:1. If a significant amount of
20   dicarboxylic acids is desired, the molar excess of carbon
monoxide relative to hydrogen is higher than 5.

The molar ratio of unsaturated carboxylic acid
to platinum as a rule is between 100:1 and 1000:1 but
preferably between 400:1 and 600:1.

25   The molar ratio of unsaturated carboxylic acid
and water as a rule lies between 1:20 and 1:2.

Next to water other solvents may optionally be
present. Examples of other solvents are dimethylformamide,
tetrahydrofuran, benzonitril and acetonitril.

30   Pentenoic acid used as starting compound for the
above hydroformylation can be 4-, 3- or 2-pentenoic acid
or mixtures of these compounds. Pentenoic acid can
advantageously be prepared by carbonylation of butadiene
and water as for example described in EP-A-405433.

35   As explained before the water obtained in the
extraction (18) and ε-caprolactam preparation (20) can be
advantageously be reused in the extraction (10) and

cyclization (22). The organic solvent obtained in the extraction (6) and (14) can be advantageously be reused in the hydroformylation extraction (4) and (12). Optionally these streams can be subjected to an additional
5   purification.

The invention will be elucidated with the following non-limiting examples.

Examples IA-Ib and comparative Experiment A were performed with methyl tert-butylether, butylacetate and
10   toluene.

For the calculation of their A and B's the following solvent properties were used:

	UNIT	MTBE	BUTYL-ACETATE	TOLUENE
T_b	°C	56	126	110
ρ	kg/m^3	745	876.1	867
n_d	-	1.37	1.39	1.50
ε_r	-	3.672	6.0	2.379
δ_d	MPa$^{\frac{1}{2}}$	14.5	15.8	18.0
δ_p	MPa$^{\frac{1}{2}}$	2.9	3.7	1.4
δ_h	MPa$^{\frac{1}{2}}$	5.1	6.3	2.0
δ	MPa$^{\frac{1}{2}}$	15.8	17.4	18.2
μ	Debye	1.28	1.84	0.31
$E_{T(30)}$	kcal/mol	35.5	38.0	33.9
A	-	-2.21	-1.09	-1.95
B	-	1.70	0.62	-1.28

30   <u>Example Ia</u>

A mixture of 2.25 g 5-formylvaleric acid (17 mmol), 0.21 g 3-formylvaleric acid (1.6 mmol) and 0.50 g 4-formylvaleric acid (3.8 mmol), 0.86 g pentenoic acid (8.6 mmol), 0.7 g valeric acid (6.8 mmol) and 47 g water in which the mixture had a total volume of 50 ml, was contacted at 22°C with 50 ml methyl tert-butyl ether (MTBE) for 2 minutes. The two phases were separated by phase separation and analyzed by gas chromatography.

	water	MTBE
5-formylvaleric acid [1]	50%	50% (=100%)
3-formylvaleric acid	35	65
4-formylvaleric acid	36	64
3-pentenoic acid	13	87
valeric acid	12	88

[1] percentage of the original amount in the respective phases.

Example Ib

Example Ia was repeated with the same weight amount of butylacetate instead of MTBE:

	Water	Butylacetate
5-formylvaleric acid	48	52 (= 100%)
3-formylvaleric acid	31	69
4-formylvaleric acid	31	69
3-pentenoic acid	4	96
valeric acid	5	95

Comparative experiment A

Example I was repeated with toluene instead of MTBE. The results were:

	water	toluene
5-formylvaleric acid	87	13 (= 100%)
3-formylvaleric acid	87	13

4-formylvaleric acid	85	15
3-pentenoic acid	16	84
valeric acid	15	85

5   As is clear from Examples Ia, Ib and comparative
experiment A, the use of toluene does not result in a
separation of the 5-formylvaleric acid from the 3- and 4-
formylvaleric acid, and that separation activity is
observed when MTBE and butylacetate are used as organic
10   solvent. Furthermore, these experiments show that in order
to obtain subtantially pure 5-formylvaleric acid, several
extraction stages are necessary. Therefore, it appears
advantageous, to perform the invention in a continuous
multi stage extraction.

15

Example III

The following were weighed into a 150-ml
Hastalloy C autoclave: 37.4 mg (0.1 mmol) of $CODPtCl_2$ (COD
= 1,5-cyclooctadiene) and 89.7 mg (0.1 mmol) of
20   tetrasulphonated trans-1,2-bis(diphenylphosphino-
methylene)cyclobutane in 45 ml of degassed water. After
half an hour of stirring, 5.3 g of freshly distilled 3-
pentenoic acid was added and the autoclave was heated to
100°C at 5.0 MPa with CO/H_2 = 1 (mol/mol). The final
25   pressure was adjusted to 8.0 MPa with the CO/H_2 gas
mixture. After 4 hours the reaction mixture was cooled.
The pressure was relieved after the reaction mixture had
cooled down. The aqueous reaction mixture was then
extracted with MTBE (3 x 50 ml) under a nitrogen
30   atmosphere. After this first cycle the ether phase was
analyzed by GC. The amounts of products and starting
materials in the ether layer are given in Table 1.
Hereafter, an amount of fresh 3-pentenoic acid was added
to the aqueous phase (Table 1, column 1), whereupon the
35   reaction was repeated in the manner described above. This
cycle was repeated five times. The etheral extract was
analyzed by GC after each cycle. After the last cycle the

water phase was also analyzed by GC.

Table 1 shows the amounts of 3-pentenoic acid and the
results of each cycle. These results indicate that the
catalyst can readily be reused while retaining its
5   activity.

        The total conversion after 4 cycles was 78.8%.
The selectivity for valeric acid was 6.2%, for 5-
formylvaleric acid 62%, for total formylvaleric acids
80.3%, for dicarboxylic acids 11.4%. N/Br was 3.4.
10

Example IV

        In a laboratory a glass pilor column, 0.05 m in
diameter and 4.5 m in height, was modified so as to
accomplish a fractional extraction separation of 5FVA from
15   3- and 5-formylvaleric acids:
An inlet point for the curde formylvaleric acid was placed
about 3 m from the bottom of the glass column, an inlet
for a fresh MTBE stream provided about 0.20 m from the
bottom of the column and an inlet for water provided about
20   0.20 m from the top of the column. The bottom of the glass
column itself was adapted for removal of the aqueous phase
and the top of the column fitted for removal of the MTBE
phase.
The column as packed with 12 mm ceramic Raschig rings. To
25   be able to controll the interfacial mass-transfer area a
pulsator was attached to the bottom of the column to
generate an up and down movement of the total liquid
content of the glass column. Both the amplitude and the
frequency of the pulsation could be varied as a means of
30   controlling the energy dissipation in the extraction
column.
An acid mixture as obtained in Example III, consisting of
3.25 kg/h MTBE, 1.17 kg/h 5FVA, a total of 1.40 kg/h 3-
and 4-formylvaleric acids, 0.23 kg/h pentenoic acid and
35   0.46 kg/h dicarboxylic acids, the pure MTBE and the pure
water were fed continuously to the column at the points
referred to above; the flow rate of pure water equaled

16.25 kg/h and the flow rate of pure MTBE equaled 6.97 kg/h.

During the operations the feed streams as well as the column were maintained at about 25°C. The frequency and
5   stroke length of pulsation were set to 90 strokes per minute and 0.01 m, respectively.

Both the organic top stream and the aqueous bottom stream were analyzed for the different acids. The weight ratio of the 5FVA to the total amounts of acids in the aqueous
10   bottom stream (the purity of the 5FVA) was about 0.98 (the other components were 3FVA and 4FVA) and the yield of 5FVA (the mass-flow rate of 5FVA in the aqueous bottom stream relative to the mass-flow rate of 5FVA in the acid feed) was about 0.98.

15

TABLE 1

3-PA added (g) (1)	cycle	PA-s (g) (2)	VA (gPa) (3)	5-FVA (gPa) (4)	FVA (gPa) (5)	dicarboxylic acids (gPa) (6)	rest (gPa)	total (gPa)	ToF (7)
5.30	1	1.16	0.25	1.85	2.51	0.34	0.04	4.30	103.3
4.84	2	0.70	0.25	2.38	3.11	0.51	0.05	4.62	103.3
4.97	3	0.76	0.26	2.72	3.52	0.52	0.10	5.17	105.0
5.97	4 (8a) (8b)	1.85 0.01	0.26 --	2.83 0.52	3.63 0.56	0.50 0.02	0.12 0.02	6.36 0.61	103.0
21.08 (9)		4.47	1.02	10.29	13.34	1.89	0.33	21.05	

	conv. (%)	sel_{VA} (10)	sel_{5-FVA}	sel_{FVA}	$sel_{dicarboxylic acids}$	sel_{rest}	mass balance	ToF
results after 4 cycles	78.8	6.1	62.0	80.3	11.4 N/Br=1.9	2.1	99.9	104

(1) : amount of 3-PA (3-pentenoic acid) added;
(2) : amount of pentenoic acid (PA) in ether layer;
(3) : amount of valeric acid (VA) in ether layer expressed in grammes of 3-pentenoic acid (gPa)
(4) : ditto for 5-formylvaleric acid (5-FVA);
(5) : ditto for total of isomeric formylvaleric acids (FVA);
(6) : ditto for dicarboxylic acids;
(7) : ToF= turn-over frequency= moles of product prepared per mole of platinum per hour;
(8a): composition of ether phase;
(8b): composition of water phase;
(9) : results of the total after 4 cycles;
(10): total selectivity (sel) for valeric acid, 5-formylvaleric acid etc. after 4 cycles

C L A I M S

1. Process to separate linear 5-formylvaleric acid from
   a mixture of 5- and 3- and/or 4-branched
   formylvaleric acids, characterized in that the
   separation is performed by fractional extraction with
   two immiscible solvents of which one solvent is an
   aqueous solvent and the other solvent is an organic
   solvent.

2. Process according to claim 1, characterized in that
   the organic solvent has the following
   characteristics:

$$-2.8 < A < -0.2 \text{ and } 0.14 < B < 2.39$$

or

$$1.7 < A < 4.0 \text{ and } -4.0 < B < -1.64$$

in which, A and B are:

$$A = 0.23 * (T_B-138.54)/62.36 +$$
$$0.24 * (\rho-935.64)/184.82 +$$
$$0.0554 * (n_d-1.4370)/0.0635 +$$
$$0.3916 * (\varepsilon_r - 15.02)/18.66 +$$
$$0.1208 * (\delta_d - 16.68)/1.738 +$$
$$0.4135 * (\delta_p - 6.11)/5.16 +$$
$$0.3462 * (\delta_h - 8.05)/6.97 +$$
$$0.4177 * (\delta - 20.69)/5.087 +$$
$$0.3370 * (\mu - 1.73)/1.20 +$$
$$0.3723 * (E_{T(30)} - 41.14)/7.61$$

$$B = -0.3009 * (T_B - 138.54)/62.36 -$$
$$0.3882 * (\rho - 935.64)/184.82 -$$
$$0.5914 * (n_d - 1.470)/0.0635 +$$
$$0.1225 * (\varepsilon_r - 15.02)/18.66 -$$

$$0.5506 * (\delta_d - 16.68)/1.738 +$$
$$0.0970 * (\delta_p - 6.11)/5.16 +$$
$$0.2291 * (\delta_h - 8.05)/6.97 +$$
$$0.0583 * (\delta - 20.69)/5.087 +$$
$$0.0381 * (\mu - 1.73)/1.20 +$$
$$0.1550 * (E_{T(30)} - 41.14)/7.61$$

in which T_B represents the normal boiling point (°C),
ρ the density measured at 20°C (kg/m^3), n_d the
refractive index (-), ε_r the di-electric constant
measured at 20°C (-), δ_d the Hansen solubility
parameter of dispersion (MPa$^{\frac{1}{2}}$), δ_p the Hansen
solubility parameter of polarity (MPa$^{\frac{1}{2}}$), δ_h the Hansen
solubility parameter of hydrogen bonding (MPa$^{\frac{1}{2}}$), δ
the Scatchard-Hildebrand solubility parameter (MPa$^{\frac{1}{2}}$)
μ the dipole moment (Debey) and $E_{T(30)}$ the Lewis
donor/acceptor property (kcal/mol).

3. Process according to claim 2, characterized in that
    $B < -1.12 * A + 0.96$ and
    $B > 0.965 * A - 1.033$.

4. Process according to any one of claims 2-3,
    characterized in that $-2.8 < A < -0.2$ and $0.14 < B < 2.39$.

5. Process according to any one of claims 1-4,
    characterized in that the fractional extraction is
    performed continuously in which initially pure water
    and initially pure organic solvent are contacted
    counter currently in various contacting stages in
    which the crude mixture of formylvaleric acids is
    continuously fed at an intermediate stage resulting
    in a water phase rich in 5-formylvaleric acid and an
    organic phase rich in 3-formylvaleric acid and/or 4-
    formylvaleric.

6. Process for the preparation of 5-formylvaleric acid
    wherein a mixture of 3- and/or 4- and 5-formylvaleric
    acid is prepared by hydroformylation of pentenoic
    acid and 5-formylvaleric acid is separated from 3-

and/or 4-formylvaleric acid by the process according
to any one of claims 1 to 5.

7.   Process according to claim 6, characterized in that
     the hydroformylation is performed in the presence of
     water and a water soluble catalyst system comprising
     platinum or a platinum compound and a water soluble
     organic bidentate ligand.

8.   Process to prepare ε-caprolactam in which an aqueous
     solution containing 5-formylvaleric acid, which is
     obtained by the process according to any one of
     claims 1 to 7, is (a) subjected to a reductive
     amination in which an aqueous mixture comprising 6-
     aminocaproic acid and ε-caprolactam is obtained, (b)
     cyclizing 6-aminocaproic acid in a separate step to
     ε-caprolactam at elevated temperature and (c)
     separating ε-caprolactam from the aqueous mixture.

9.   Process according to claim 8, characterized in that
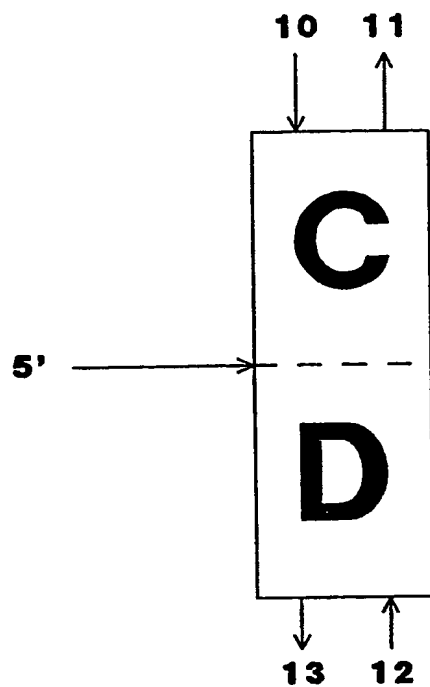   step (b) is performed using the aqueous mixture
     obtained in step (a).
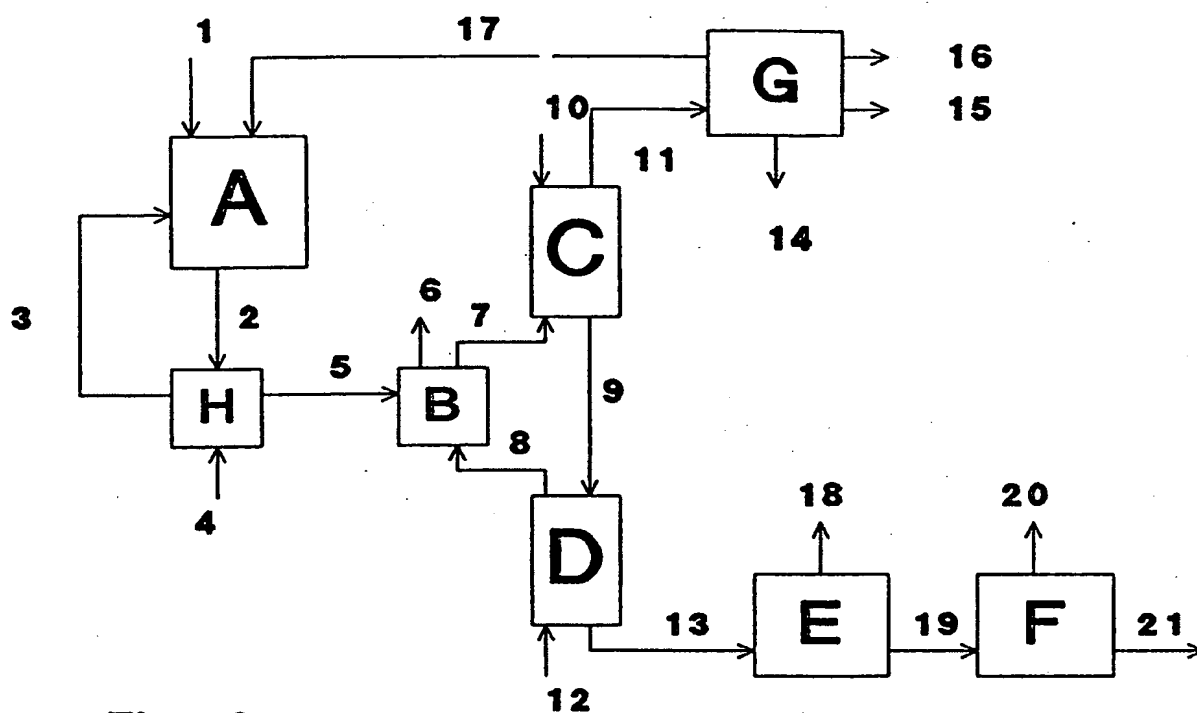
Fig. 1

Fig. 2

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6   C07C59/147   C07C51/48

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6   C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,2 204 616 (OTHMER) 18 June 1940 THE WHOLE DOCUMENT. -----	1

| | Further documents are listed in the continuation of box C. | X | Patent family members are listed in annex. |

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search	Date of mailing of the international search report
11 September 1996	19.09.96

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-2204616	18-06-40	NONE	

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